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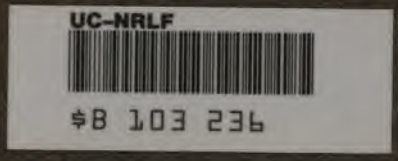

EXCHANGE

Gaylord Bros.
Makers
Syracuse, N. Y.
PAT. JAN. 21, 1908

EXCHANGE
DEC 8 1916

The Time Factor in Making Oil Gas

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE
COLUMBIA UNIVERSITY

BY
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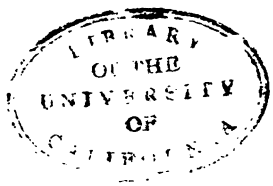

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MAY, 1915

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THE TIME FACTOR IN MAKING OIL GAS

The production of oil gas is dependent upon certain chemical laws which relate to gas reactions in general and which embody the principles of both thermodynamics and chemical kinetics.

In an investigation on the effect of the variables, temperature, pressure, and concentration on the thermal decomposition of petroleum and petroleum distillates, Whitaker and Rittman[1] have carefully considered the theoretical principles of thermodynamics as applied to gas reactions. Their experimental results verified their theoretical conclusions and showed that the principles of thermodynamics apply to the decomposition of petroleum hydrocarbons as well as to more simple reactions.

In the above work, however, conclusions were drawn on the assumption that chemical equilibrium was attained under the experimental conditions adopted. It then became a question whether or not equilibrium was reached. Undoubtedly this question could be answered by the application of the principles of chemical kinetics, which introduced the time factor. In the present study of oil gas production, therefore, four variables—time, temperature, pressure and concentration—are recognized.

Difficulties were foreseen, however, in the accurate adjustment of the above variables in commercial plants and a basis for control was sought which would fall within the range of engineering requirements. Under constant temperature and pressure conditions, the time factor, which can be controlled by variation of the rate of oil feed, offers the most available means for the study of the thermal decomposition of petroleum and petroleum distillates on the basis of the principles of chemical kinetics.

Design of apparatus is fixed for any one construction and hence remains a constant factor while the variables are controllable within certain operating limits.

[1] *J. I. E. C.*, **6** (1914), 383, 472.

The concentration factor above is considered in the sense of changes involved in the admixing of other substances with the initial material, such as the decomposition of oil in an atmosphere of hydrogen, carbon monoxide; etc.

THEORETICAL

According to chemical kinetics, a reaction tending toward a state of equilibrium will require time to reach such a state.

A reversible reaction may be represented thus:

$$n_1A_1 + n_2A_2 \rightleftarrows n_1'A_1' + n_2'A_2' \ldots$$

Such an equation represents two reverse reactions, each with a separate reaction velocity:

$$v = k(A_1)^{n_1}(A_2)^{n_2} \ldots \qquad v' = k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots$$

The difference between these two velocities at any moment of time under constant conditions will give a certain change per unit of time in one direction or the other toward equilibrium. This change per increment of time, $\frac{dx}{dt}$, is commonly shown as follows:

$$\frac{dx}{dt} = v - v' = k(A_1)^{n_1}(A_2)^{n_2} \ldots . - k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots$$

in which k and k' are the velocity constants of the two reverse reactions, (A_1), (A_2), etc., are the concentrations of the reacting substances, and n_1, n_2, etc., their respective molecular exponents as obtained from a properly balanced equation.

The above velocity constants vary with temperature[1] and as a result temperature has a very marked effect upon the reaction velocities of the two reverse reactions. The effect of temperature on a number of gas reactions has been very carefully studied by Bodenstein[2] and the fundamental equations applied mathematically to the experimental results.

At equilibrium, the velocities of the opposing reactions are equal and hence the change per increment of time, $\frac{dx}{dt}$, must become zero.

$$\frac{dx}{dt} = v - v' = k(A_1)^{n_1}(A_2)^{n_2} \ldots - k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots = 0$$

Hence,
$$\frac{k}{k'} = \frac{(A_1')^{n_1'}(A_2')^{n_2'} \ldots}{(A_1)^{n_1}(A_2)^{n_2} \ldots} = K,$$

[1] Trautz, *Z. Elektrochem.*, **18** (1912), 513; *Z. physik. Chem.*, **68** (1909). 295; **74** (1910). 747; Zellinek, *Z. anorg. Chem.*, **49** (1906), 229.

[2] Bodenstein, *Z. physik. Chem.*, **29** (1899), 147, 295, 315, 429, 665; Bodenstein and Wolgast, *Ibid.*, **61** (1908), 422.

where K is the equilibrium constant. Thus chemical equilibrium deals only with the end state of a reaction and time is not a factor.

Where time is not considered the relations between the state of equilibrium and the thermal values of a reaction can be worked out by the application of thermodynamics. Such relations have been developed by Nernst,[1] Mayer and Altmayer.[2] and others[3] and expressed in terms of mathematical formulas from which equilibrium compositions can be calculated: *e. g.*, the Nernst approximate formula:

$$\log K_p = \log \frac{p_1'^{n_1'} p_2'^{n_2'} \ldots}{p_1^{n_1} p_2^{n_2} \ldots}$$

$$= \frac{Q_p}{4.751 T} + 1.75(\Sigma n' - \Sigma n) \log T + (\Sigma n' C' - \Sigma n C)$$

By the use of such formulas the ultimate composition representative of equilibrium conditions is obtained. This final composition, according to the principles of chemical kinetics, represents the end point of a reaction which can be attained only through a sufficient lapse of time. As applied to the production of oil gas, a progressive decomposition, in which time is an important factor, should proceed to an ultimate state of equilibrium.

The reactions taking place in the decomposition of petroleum hydrocarbons by heat are numerous and not definitely known. In the industries based on these decomposition reactions, as in the making of oil gas, carbureting water gas, and cracking petroleum for light distillates, the chemical nature of only the initial materials and the final products are determined, and this does not give any definite knowledge concerning the intermediate reactions. The breaking down of hydrocarbons of high molecular weights to simpler hydrocarbons apparently consists in numerous consecutive and concurrent reactions,[4] but their actual course from the initial material to the final products has not been established. Even in the absence of

[1] W. Nernst, "Theoretische Chemie."

[3] Mayer and Altmayer, *Ber.*, **40** (1907), 2134.

[2] H. von Wartenberg, *Z. physik. Chem.*, **61** (1907), 366.

[4] Berthelot, *Ann. chim. phys.* (**1866** to **1877**); Thorpe and Young, Liebig's *Ann.*, **165** (1872), 1; *Proc. Roy. Soc.*, **21** (1873), 184; Norton and Andrews, *Am. Chem. J.*, **8** (1886), 1; Armstrong and Miller, *J. Chem. Soc.*, **49** (1886), 74; Lewes, *J. Soc. Chem. Ind.*, **11** (1892), 584; Haber, *Ber.*, **29** (1896), 2691; *J. Gasbel.*, **34**, 377, 435, 452; Worstall and Burwell, *Am. Chem. J.*, **19** (1897), 815; Bone and Coward, *J. Chem. Soc.*, **93** (1908), 1197; Hempel, *J. Gasbel.*, **1910**, p. 53; Kramer and Spilker, *Ber.*, **33** (1910), 2265; Lewes, *Trans. Chem. Soc.*, **69** (1892), 322; *Proc. Roy. Soc.*, **55** (1894), 90; **57** (1905), 394, 450; Bone, *J. Gasbel.*, **51** (1908), 803; Engler, *Ber.*, **30** (1897), 2908.

such knowledge, the theoretical principles of chemical kinetics which apply to single reactions should also hold in the case of the numerous reactions involved in the thermal decompositions of petroleum hydrocarbons.

The importance of the variable time in a few related decompositions has been shown by a number of investigators. Lewes[1] finds that the decomposition of ethylene is dependent not only upon temperature and pressure but also on rate of flow. Clement[2] has shown the importance of the time factor in the manufacture of producer gas. Hempel's[3] experiments with gas oils at temperatures between 700 and 900° C. have demonstrated further the influence of the rate of oil feed upon the composition of the products. J. F. Tocher[4] has also shown some results of a change in the rate of oil feed. A technical application of the time factor can be found in the experiments of Jones.[5]

In varying the rate of oil fed into a retort or furnace for the production of oil gas, one varies the time during which any portion is heated and hence the time allowed for the reaction. With a very slow rate of oil feed, the reaction would attain an equilibrium composition representative of the heating zone conditions. With increasing rates of oil feed the time allowed for reaction is shortened and the products obtained correspond to an earlier stage of the decomposition. The composition of oil gas is therefore dependent upon the time allowed for chemical change. Hence the study of the time factor in the making of oil gas should yield interesting and practical results.

EXPERIMENTAL CONSIDERATIONS

A study of the reactions of gases moving through heated vessels, the method which was used in this investigation and is representative of practice in oil gas production, involves certain features of design which are dependent upon the theoretical considerations of reaction velocity. During the passage of any heating-zone-composition through the cooling zone, there will be a certain change in composition due to a reversal of reactions.[6] The extent of this reversal will depend on the time required in the cooling zone

[1] Lewes, *Proc. Roy. Soc.*, **55** (1894), 90; **57**, 594.
[2] Clement, *Bull.* **30** (1909), D. of Ill. Eng. Exp. Sta.
[3] Hempel, *J. Gasbel.*, **1910**, pp. 53, 77, 101, 137 and 155.
[4] J. F. Tocher, *J. Soc. Chem. Ind.*, **13** (1894), 231.
[5] Jones, *Am. Gaslight J.*, **99** (1913), 273.
[6] Nernst, *Z. anorg. Chem.*, **49** (1906), 213.

to arrest the reactions. Hence the more quickly these gases are cooled after leaving the heating zone, the more nearly will the product obtained be representative of the heating zone conditions. The efficiency of the cooling zone in arresting the reversal of reactions is materially increased in some of the decomposition reactions by the separation of carbon in the solid phase, making it possible to obtain as the product a gas mixture which very closely approximates the composition of the mixture in the heating zone. It is thus evident that reaction velocity is important not only in the heating zone, but also in the cooling zone.

Further essential considerations in the attainment of a product representative of heating zone conditions are those of convection and diffusion. As shown by Langmuir,[1] diffusion and convection act in a way that is equivalent to decreasing the reaction velocity. Convection currents may be set up by differences in temperatures or irregularities in design, the results of which will tend to shorten the time of contact for some of the molecules in the heating zone. The effect of diffusion increases with temperature as the coefficient of diffusion varies approximately with the square of the absolute temperature. Considering the heating zone or cooling zone separately, raising the temperature increases the diffusion effect and is in a sense equivalent to shortening the time of contact. This effect may be a material consideration in the heating zone but would be almost negligible in the cooling zone. On the other hand, when one considers the mutual effect of the two zones, diffusion offers an advantage, due to the differences in the partial pressures of the reacting substances. Differences in partial pressures cause those substances whose proportions increase with rise in temperature to diffuse from the heating zone to the cooling zone and *vice versa* those substances whose proportions decrease with rise in temperature diffuse in the opposite direction. Hence, this effect aids also in obtaining products more nearly corresponding to the heating-zone-composition.

OIL GAS APPARATUS

The design and construction of an apparatus suitable for carrying out the study of the behavior of hydrocarbon vapors under the conditions outlined in the foregoing theoretical discussion involved many im-

[1] Langmuir, *J. Am. Chem. Soc.*, **30** (1908), 1742.

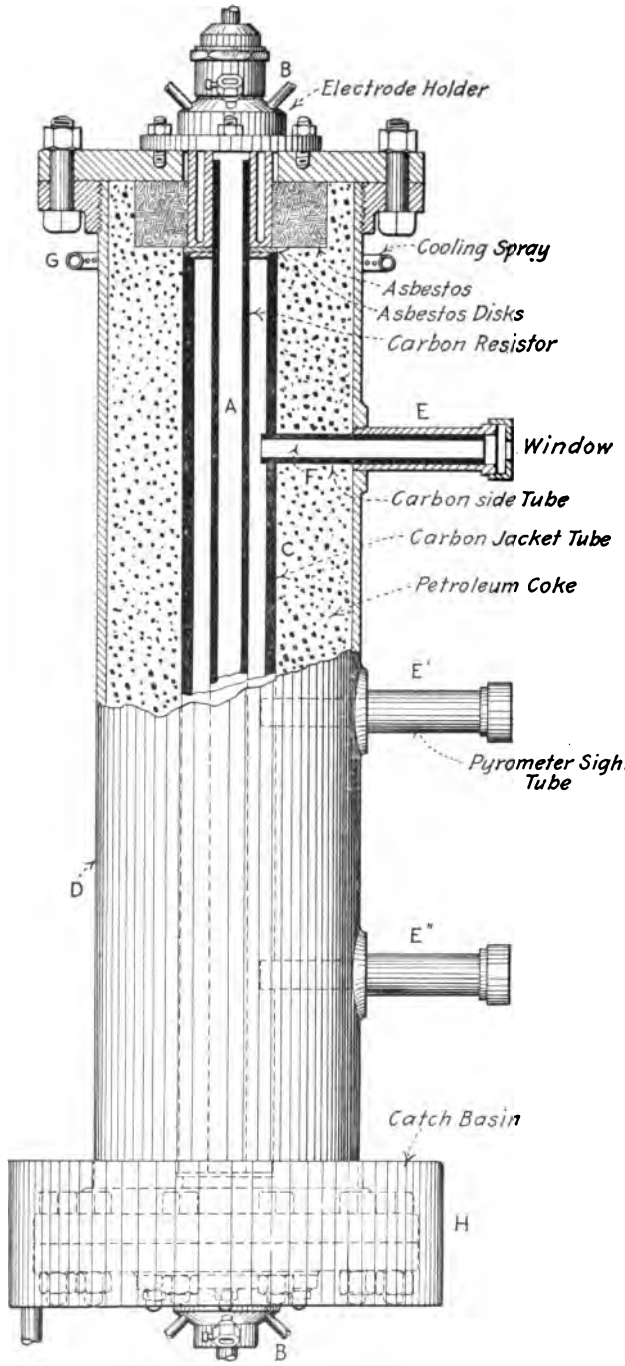


FIG. I—RESISTANCE FURNACE

portant considerations. In such an apparatus it was desired to provide for working with constant temperatures up to 2300° C.; for pressures ranging from —15 lbs. to 100 lbs. gauge per sq. in.; for constant rates of oil feed over a large range; for suitable means of collecting the resultant products; and for numerous other requirements.

THE FURNACE

An electrically heated carbon tube resistance furnace, illustrated in Fig. I, was constructed. This furnace embodies the use of a carbon tube resistor

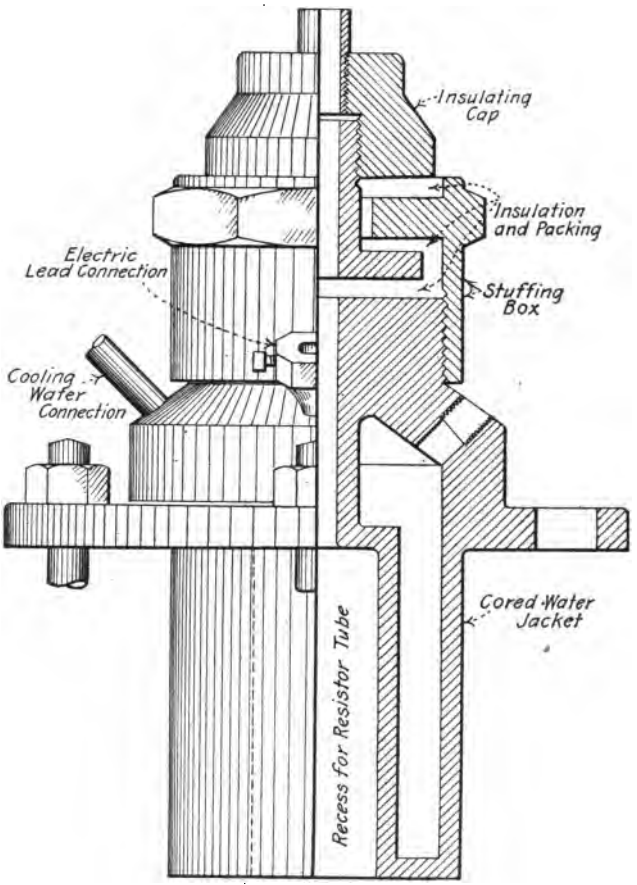


FIG. II—ELECTRODE HOLDER

held by water-jacketed electrode holders and surrounded by heat-insulating material enclosed by an iron furnace body which is provided with suitable accessory mechanisms for electrical and water-cooling

connections, feed and discharge apparatus, and observation of temperatures and pressures.

The carbon tube[1] resistor (A) is 46 in. long, 1 in. inside diameter, with 0.25 in. wall. Deducting the electrode holder contact length, about 4 in. at each end, this gives a heating zone of 38.5 linear inches with 120 sq. in. heating surface and a volume equal to 30.5 cu. in. or about 500 cc. This tube is copper plated externally at each end to give a suitable contact surface of 18 sq. in. with each electrode holder.

The electrode holders (BB) are integral bronze castings with cored water jackets and with flanges for bolting to the furnace heads. The construction is shown in some detail in Fig. II. Into the main body of the holder outside of the flanges, are drilled and tapped the water-jacket connections and binding posts for the electric leads. The outside ends are further provided with carefully insulated stuffing boxes and caps in order to separate the heating element, electrically, from the feed and discharge mechanisms of the assembled apparatus. The flanges, bolts, and nuts are insulated with sheet mica to isolate the heating element from the furnace casing.

The resistor tube is surrounded by a large concentric carbon tube (C), 3 in. inside diameter and 0.50 in. wall, which is insulated from the electrode holders by asbestos disks. This construction leaves an annular dead gas space of 0.75 in. around the resistor. Between this large carbon tube and the furnace casing powdered petroleum coke is packed for heat insulation.

The furnace body (D) is made from extra heavy wrought iron pipe with screwed and peened flanges at each end. To these are bolted blank companion flanges centrally bored to receive the bodies of the electrode holders and faced to seat the flanges. The electrode holders are each held in position by six 0.5 in. stud bolts drilled and tapped into the furnace heads. As above stated the mountings of the electrode holders are mica-insulated from any contact points with the furnace casing. Three solid bosses, 3 in. diameter by 0.5 in. thick, are autogenously welded on the outside walls of the furnace casing and are drilled and tapped for 1 in. brass extensions which serve as sight tubes (EE'E").

These extension tubes register with and support carbon side tubes (FF'F"), 0.75 in. inside diameter and 0.125 in. wall, which connect the sight tubes with

[1] Carbon tubes were obtained from the National Carbon Co.

the annular space around the resistor. The outer ends of the sight tubes are provided with glass windows 0.25 in. thick. This combination gives a straight way view into the resistor chamber at three points along its length.

The water-cooling system for the furnace casing consists of a perforated yoke of water pipe (G) at the top for spray cooling and an annular catch basin (H) at the bottom.

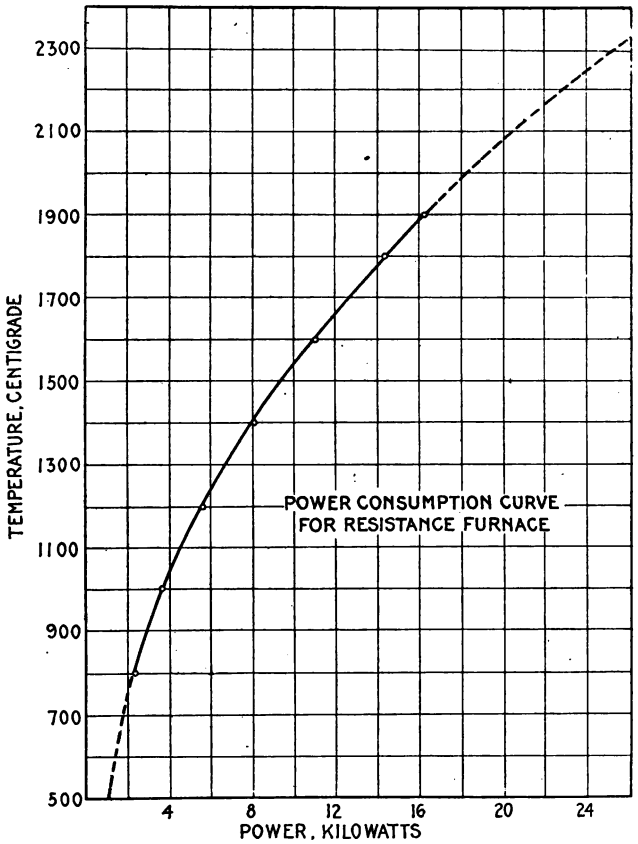


FIG. III—POWER CONSUMPTION CURVE FOR RESISTANCE FURNACE

OPERATION AND TEST OF FURNACE

The power required to heat the furnace is derived from a single phase, 60 cycle, 50 kw. alternating current generator, having a range of 5 to 100 volts which can be regulated within narrow limits by a switchboard and rheostat combination. Thus the temperature of the furnace can be readily controlled. Power was measured by the use of a portable Weston ammeter,

voltmeter, and wattmeter placed in close proximity to the furnace. The readings from these three instruments made it possible for the operator to determine the power consumption of the furnace and to check the proper working of the apparatus.

Ordinarily it required about an hour to heat the furnace to a constant temperature after the power had been turned on. The high temperatures are measured by sighting through the observation tube windows with a Wanner optical pyrometer; no temperature corrections are necessary. The low temperatures are measured by replacing the glass windows by small stuffing boxes through which pyrods are inserted. The power used for the various temperatures is shown in Fig. III. This furnace has been tested at various temperatures ranging from 500 to 2300° C. and held constant at such temperatures for several hours at a time. In these tests the readings at the three different observation points agreed. In one of the tests the furnace was held at 1600° C. for four hours without requiring any regulation of the power. A hydrostatic pressure test to 200 lbs. per sq. in. was made on the assembled furnace with the feed and discharge mechanisms attached.

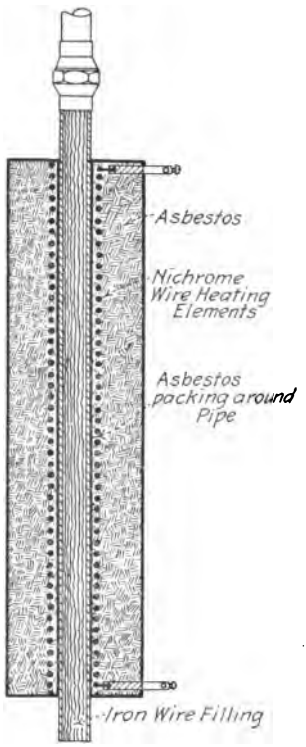


FIG. IV—PREVAPORIZER

The carbon resistor is the only part of the furnace which requires renewal. Yet a single tube has been used for fifty runs at various temperatures. Whenever it is necessary to renew the resistor, the electrode holders are removed and a new tube fitted.

PREVAPORIZER

The object of the prevaporizer is to vaporize the oil before it enters the heating zone of the furnace.

The prevaporizer, Fig. IV, consists in a $^3/_8$ in. brass

pipe 18 in. long, containing a bundle of iron wire for spreading the oil. It is electrically heated from the outside by 8 turns to the inch of No. 18 B. & S. nichrome resistance wire properly insulated from the tube by four wrappings of asbestos paper. For heat conservation the whole is surrounded by standard 85 per cent

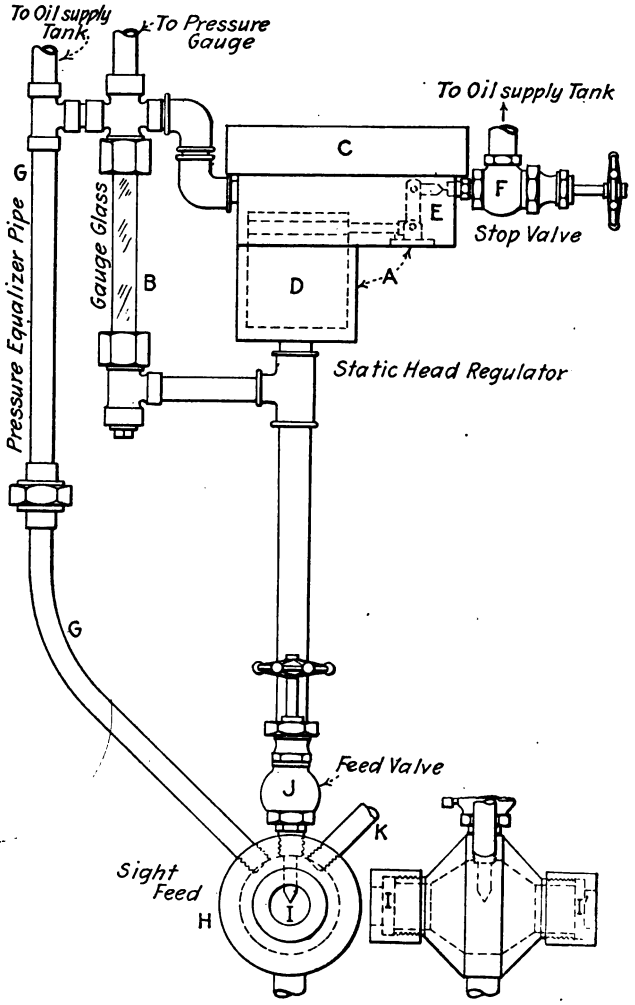


FIG. V—STATIC HEAD AND FEED REGULATOR

magnesia pipe covering. The power required for heating the prevaporizer is furnished from a separate direct current line and regulated by the use of a lamp bank.

Prevaporization was found to be an essential feature as experiments showed that even when the heating

zone temperature of the furnace was 1400° C. and the rate of oil feed 50 drops per minute, the oil dropped directly through the heated carbon tube and came out at an equal rate with very little vaporization; this result was apparently due to spheroidal effect and lack of contact with the heated surface. With a solid or vapor passing through the tube under the same conditions, the solid would become heated by radiation and the vapor mainly by conduction. Prevaporization was found to be incomplete at very high rates of oil feed, *i. e.*, the prevaporizer has a maximum capacity. As an additional precaution, at high feed rates, the wire filling of the prevaporizer was extended into the heating zone of the furnace.

STATIC HEAD AND FEED REGULATOR

The object of the static head and feed regulator is to provide for an accurate and steady rate of oil feed which in turn controls the time factor.

The static head regulator, shown in Fig. V. is made up of a specially designed cast brass casing. A, with a gauge glass, B, and a screw cap, C, which may be removed for internal adjustment. The inside mechanism consists of a cork float, D, which operates a needle valve, E. This constant level regulator is also connected with the oil supply tank, the feed mechanism, the pressure equalizer pipe, and the pressure gauge. Valve F is a stop-valve to be closed when the apparatus is not in use.

The sight feed regulator H is constructed from a brass casting provided with two glass windows, II', and an angle needle valve, J, to regulate the rate of oil feed. Connections are made from this with the static head regulator, prevaporizer, and pressure equalizer and admixture pipes as shown in Fig. V.

A constant head of oil is necessary in order that a fixed opening of the feed valve J may give a definite and uniform rate of oil feed. This is accomplished by the cork float D operating the needle valve E, which admits oil from the storage tank at a rate equal to the rate of feed. In order to insure the proper working of this mechanism, a gauge glass, B, is provided, which registers the oil level. This level has been found to vary not more than $^1/_8$ in. regardless of the level in the oil supply tank. The oil feed is regulated to the desired rate by adjusting the needle valve J, according to observations made through the windows I.

Table I contains data taken from some of the experimental runs and serves to show the range of accuracy of oil feed obtained by this mechanism:

TABLE I—RANGE OF ACCURACY OF OIL FEED

Test	Rate of feed per minute	Period of test	Variation
1.....	8 drops	3 hrs.	None
2.....	100 drops	2 hrs.	1 drop
3.....	5.4 cc.	1 hr.	None
4.....	15.8 cc.	30 min.	0.5 cc.
5.....	69.0 cc.	8 min.	None

The pressure of the whole system is equalized by a pressure equalizing pipe, G, which communicates the furnace pressure through the sight feed to the static head regulator and the oil supply tank.

Pipe K is used for recirculating the gases made or for admixing other material with the oil.

OIL SUPPLY TANK

The oil supply tank (see Fig. VI), with a capacity of 600 cc., is made from standard 1.5 in. brass pipe and fittings. To this a gauge glass is connected and provided with a parallel meter stick carrying a sliding pointer. This arrangement is calibrated for volume and enables the operator to verify the uniformity of the rate of oil flow and hence the accuracy of the constant head apparatus.

GAS HOLDERS

The gas holders are balanced bell holders with water seal. These are calibrated and provided with a meter stick and pointer in order to facilitate the recording of the rate of gas generation during a run.

FEED AND DISCHARGE MECHANISM

Both the oil feed mechanism and the condensing system are carried on the supporting framework by swinging arms. The connections to the furnace at their respective ends are made through ground joint unions. When cleaning, renewals or repairs to the furnace are necessary, the unions may be disconnected and the mechanism swung aside without disturbing the furnace.

ASSEMBLY AND OPERATION

The arrangement of the complete apparatus ready for operation is shown in Fig. VI. At the beginning of an experiment the oil tank is first filled with oil; after the feed valve has been adjusted to the desired rate of oil feed, oil-tank readings are taken at definite intervals of time.

The oil passes from the supply tank to the static

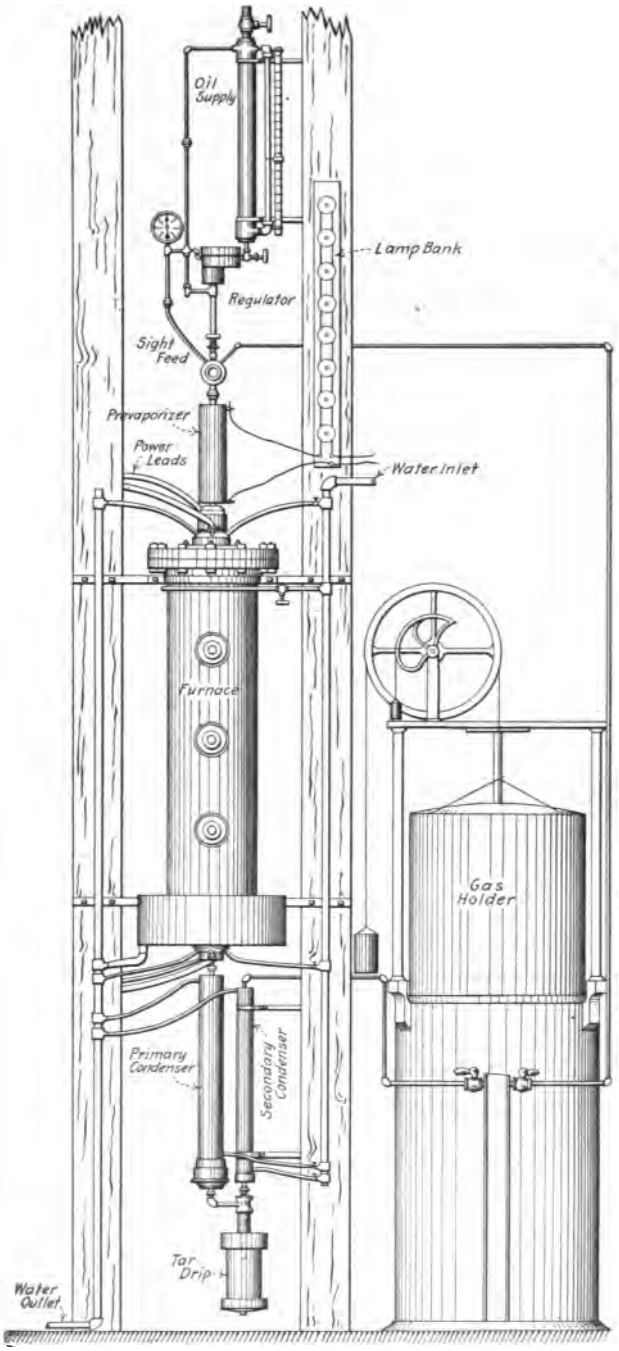


FIG. VI—OIL GAS APPARATUS

TABLE II—RECORDS OF RUNS AT DIFFERENT RATES OF OIL FEED

SLOW RATE OF OIL FEED

Time	K. W.	Temp. ° C.	Gauge pressure Lbs. per sq. in.	Oil rate Cc. per min	Gas rate Liters per min.
11.15	4.0	1010	0	2.1	...
11.20	...	....	0	2.1	2.0
11.25	...	1000	0	2.0	1.9
11.30	...	....	0	2.0	1.7
11.35	...	....	0	2.1	1.8
11.40	...	1000	0	2.2	1.8
11.45	...	....	0	2.0	1.9
11.50	4.1	....	0	2.1	1.8
11.55	...	1010	0	2.2	1.8
12.00	...	....	0	2.1	1.8
12.05	...	1000	1	2.1	1.7
50 min.				105 cc.	92 liters

PERCENTAGE GAS ANALYSIS—SLOW RATE OF FEED—MARCH 8, 1915

	CO_2	Ill.	O_2	CO	H_2	C_nH_{2n+2}	N_2 (diff.)	Total	Carbon	Tar
	0.6	6.7	0.8	1.0	54.5	29.0	7.4	100	Little	Trace
or	...	7.5	...	...	60.5	32.0	...	100	.....	.....

MODERATE RATE OF OIL FEED

Time	Temp., ° C.	Gauge pressure Lbs. per sq. in.	Oil rate Cc. per min.	Gas rate Liters per min.
4.10	1000	0	14.0	...
4.12	....	0	13.5	5.8
4.14	....	0	13.5	5.8
4.15	....	0	13.0	6.2
4.20	....	0	13.5	6.5
4.25	....	0	13.5	5.3
4.30	....	0	13.5	6.3
4.35	1000	0	13.0	6.5
25 min.			240 cc.	160 liters

PERCENTAGE GAS ANALYSIS—MODERATE RATE OF FEED—APRIL 16, 1915

	CO_2	Ill.	O_2	CO	H_2	C_nH_{2n+2}	N_2 (diff.)	Total	Carbon	Tar
	0.1	19.2	0.0	0.8	44.3	35.2	0.4	100	Little	125 cc.
or	...	19.5	...	...	44.8	35.7	...	100	....	...

RAPID RATE OF OIL FEED

Time	Temp. ° C.	Gauge pressure Lbs. per sq. in.	Oil rate Cc. per min.	Gas rate Liters per min.
3.30	1000	0	44.0	....
3.32	....	0	44.5	13.0
3.36	....	0	44.5	13.2
3.38	....	0	45.0	13.3
3.41	1000	0	44.5	13.3
11 min.			490 cc.	445 liters

PERCENTAGE GAS ANALYSIS—RAPID RATE OF FEED—APRIL 16, 1915

	CO_2	Ill.	O_2	CO	H_2	C_nH_{2n+2}	N_2 (diff.)	Total	Carbon	Tar
	0.0	35.0	0.6	1.8	21.8	36.0	4.8	100	Trace	245 cc.
or	...	37.7	...	...	23.5	38.8	...	...	.....	...

head regulator and out through the feed adjusting valve to the prevaporizer. From here the vaporized oil is carried directly into the heating zone of the furnace.

The oil gas runs were made over a range of constant temperatures from 800° to 1600° C.

Temperature observations, during a run, showed that the feed end of the resistor was 50° to 100° C. cooler than the center and discharge points which remained practically the same. This lower temperature of the feed end of the reaction chamber is obviously due both to the heating up of the oil vapors and to the large amount of heat required for the endothermic reactions taking place in this part of the tube. Further-

more, the deposition of carbon here may reduce the resistance and hence lower the temperature.

The measurement of the high temperatures by the optical pyrometer offered no difficulties as there were no fumes present in the furnace.

The hot gases are discharged from the reaction chamber directly into the primary condenser where the reactions are arrested by the cooling. From here the gases go through the tar drip which is followed by a secondary condenser and thence out to the gas holders, where the rate of gas generation is noted at definite intervals of time. The condensates from both the primary and secondary condensers run into the same tar drip from which they may be readily removed at the end of each experiment.

Typical records of runs are shown in Table II.

GAS SAMPLING AND ANALYSIS

The gas from the runs was collected in the balanced bell gas holders already described. Care was always taken to saturate the seal water with a similar gas previous to the collection of the run from each experiment. Before taking a sample of gas from the holders for analysis, the product was allowed to stand a sufficient length of time for complete mixing by diffusion and for the settling out of any tar or carbon that might have been carried over.

The gas samples were analyzed by the standard methods[1] with a few modifications to meet special requirements. The Hempel equipment was used in all analyses and the order of procedure was as follows:

1—Absorption of the carbon dioxide with KOH solution.

2—Absorption of the illuminants with fuming sulfuric acid (23 per cent free SO_3).

3—Absorption of the oxygen by alkaline pyrogallol.

4—Absorption of the carbon monoxide by two ammoniacal cuprous chloride solutions.

5—Partial combustion of the hydrogen by passing 20 to 30 cc. of the remaining gas mixed with the proper proportion of pure oxygen over palladium black heated to 70° to 80° C.

6—Explosion of the remaining hydrocarbon-oxygen mixture.

The partial combustion of hydrogen in gas mixtures containing percentages above 90 per cent was difficult on account of the danger of explosion. In such cases the mixture was exploded directly and calculated as hydrogen and methane from the formulas,

[1] Dennis, "Gas Analysis," 1913.

cc. of $H_2 = \frac{2T.\ C. - 4CO_2}{3}$ and cc. of $CH_4 = CO_2$,

where T. C. = total contraction noted directly after the explosion and CO_2 = contraction due to absorption with KOH after explosion.

In the partial combustion of hydrogen followed by the explosion of the residual gas mixture, it was often difficult to obtain an explosion by using air as the source of oxygen. This difficulty was avoided, however, by the use of pure oxygen in such an amount that, after the removal of the hydrogen by the palladium black treatment, an explosive mixture remained.

From the total contraction and the carbon dioxide found by explosion, the volume of saturated hydrocarbons was calculated by the following formula:[1]

$$V = \frac{2T.C. - CO_2}{3}$$

This gave the total volume of all the saturated hydrocarbons: methane, ethane, propane, etc. From the V and the CO_2 a mean value of n for the type formula C_nH_{2n+2} was obtained, which gave an indication of the nature of the hydrocarbons present, that is, $n = \frac{CO_2}{V}$.

There is no proof that the saturated hydrocarbons do not contain hydrocarbons of higher molecular weight than ethane. The true percentages of each of the C_nH_{2n+2} hydrocarbons can be determined only by the fractional distillation methods of Burrell[2] and his associates, of the U. S. Bureau of Mines.

In common analytical practice, when the hydrogen is separated by partial combustion, the remaining gas is assumed to contain only methane and ethane and is calculated as such. This obviously would give an error dependent upon the amount of heavier hydrocarbons present.

For the calculation of the respective volumes of ethane and methane present on the above assumption, the following formulas were used:

cc. of $C_2H_6 = \frac{4CO_2 - 2\ T.\ C.}{3}$ and

cc. of $CH_4 = CO_2 - 2\ C_2H_6$.

[1] DeVolderc and DeSmet, *Z. anal. Chem.*, **49** (1910), 661.

[2] Burrell and Seibert, *J. Am. Chem. Soc.*, **36** (1914), 1537; Burrell and Robertson, *J. I. E. C.*, **7** (1915), 17, 210.

THE TIME FACTOR

The experimental values found in this investigation are considered on the assumption that the true time factor is a function of the rate of oil feed. As stated above, the true time factor, which represents the interval of time in which the reactions progress, is dependent upon the theoretical considerations of reaction velocity. It is substantially a function indirectly proportional to the rates of oil feed; *i. e.*, an increase in the rate of oil feed decreases the time of reaction.

On the other hand, the rate of gas production might be considered as a means of obtaining a better approximation of the true time factor. This would necessitate the calculation of the volumes of the gases to the reaction zone conditions. Furthermore, tars would have to be considered, in case of their formation. Such a method, even if both tars and gases were considered, would not give a value approximating the true time factor, as the original oil vapors occupy a much smaller volume than their decomposition products; in fact decomposition in the reaction zone proceeds with a continuous increase in volume. It is apparent then that this basis of a time factor would be impractical either for experimental study or for technical purposes. For these reasons the time factor as based on the rate of oil feed was selected for this investigation as it offers a comparative value for theoretical considerations and is an easily measured quantity, as well as a readily controllable variable for practical work.

EXPERIMENTAL

A water-white kerosene, boiling between 150–290° C., was used in all experimental runs.

All runs were made at atmospheric pressure, any variation of which was indicated by the pressure gauge.

The complete gas analyses always showed varying percentages of carbon dioxide, carbon monoxide, and air (*e. g.*, see Analyses in Table II), so that the figures for illuminants, hydrogen, and saturated hydrocarbons did not present these constituents in their proper relationships. This difficulty was overcome by recalculating the analyses to the illuminant-hydrogen-saturated hydrocarbon basis (see Analyses in Table II) and all subsequent data are presented from this view point.

EFFECT OF RECIRCULATION OF GASEOUS PRODUCTS

In this investigation it was necessary first to prove

that in the production of oil gas, chemical equilibria are not obtained, for if such were not the case, a study of the time factor would be valueless. This point was proved by runs at slow rates of oil feed, so as to allow a considerable time for reaction, and subsequent recirculations of the products. Slow rates of oil feed were selected because, if equilibria were not established at such rates, it is self-evident that they would not be established at higher rates with correspondingly less time for reaction.

In experimental data given in Table III three different rates of oil feed at the same temperature, 1200° C., were selected and the recirculations (*a* and *b*) made at rates equal to their respective rates of gas

TABLE III—GAS GENERATION AND RECIRCULATION AT 1200° C.

Run No.	Oil rate Cc. per min.	Gas rate Liters per min.	GAS ANALYSES (PERCENTAGES) Illum.	H_2	C_nH_{2n+2}
1	1.1	1.25	0.0	92.5	7.5
1*a*	...	1.25	0.0	94.0	6.0
2	2.4	2.4	1.1	90.5	8.4
2*a*	...	2.4	0.0	92.8	7.2
2*b*	...	2.4	0.0	93.2	6.8
3	6.0	5.3	1.5	88.2	10.3
3*a*	...	5.3	0.5	88.9	10.1
3*b*	...	5.3	0.0	90.5	9.5

generation. Rates that gave practically no tar were selected; this was necessary because tars, if present, undoubtedly take part in the reactions in the heating zone.

A consideration of the general velocity equation in conjunction with the above data will show some interesting relations between reaction velocity and gas recirculation.

$$\frac{dx}{dt} = k(A_1)^{n_1}(A_2)^{n_2} \ldots - k'(A_1')^{n_1'}(A_2')^{n_2'} \ldots$$

Here the rate of change is dependent upon the respective velocity constants of the reverse reactions and the concentrations of the reacting substances. For any one temperature the velocity constants have a fixed value. Should the decomposition reactions have completed themselves or come to equilibrium, dx/dt would have been equal to zero, but the above data shows that this was not the case, and hence equilibrium was not attained. As the reactions approach equilibrium, the respective velocities of the two reverse reactions become more nearly equal, *i. e.*, the rate of change, dx/dt, is a decreasing function as equilibrium is approached. The results in Table III show this

effect quite conclusively, as the change in the second recirculation is less than that in the first.

In case one considers the reactions to proceed to completion in one direction only, the same theoretical conclusions hold.

In the above gas mixtures, with no illuminants present, the saturated hydrocarbon percentages were found to consist entirely of methane. The reaction involved at such a stage of the decomposition consists only in the decomposition of methane into carbon and hydrogen. The equilibrium composition of this reaction at 1200° C. (calculated according to the formulas of Nernst or Mayer and Altmayer) should show not more than 0.3 per cent methane, as has been experimentally proved by many investigators.[1] The reason that this value was not obtained in the above experiments is that sufficient time was not allowed for the reactions to reach equilibrium. The intervals of reaction time in the runs in Table III calculated from the gas rates, temperature, pressure and volume of heating zone, amounted to only a few seconds—5, $2^1/_2$ and 1 second, respectively—for Nos. 1, 2 and 3. Equilibrium compositions could be attained only by the lapse of many minutes in the heating zone. This emphasizes the fact that equilibrium compositions are not obtained in oil gas practice and further that it would be impractical to run an oil gas generator at such rates of oil feed as would even approximate equilibrium compositions.

CHANGE OF COMPOSITION WITH RATE OF OIL FEED AT CONSTANT TEMPERATURE

The changes of composition with the rate of oil feed at constant temperature are plotted from the experimentally determined data in Fig. VII. In general, these curves show that a decrease in the oil rate, *i. e.*, an increase in the time of reaction, at any one constant temperature, results in a greater degree of decomposition.

For any two temperatures that can be compared with reference to percentage of any one selected constituent, the higher temperature will result in an equivalent degree of the decomposition at a much higher rate of oil feed. However, the total compositions of the gases produced at the different temperatures are

[1] Bone and Jerdan, *J. Chem. Soc.*, **71** (1897), 41; **79** (1901), 1042; Mayer and Altmayer, *Ber.*, **40** (1907), 2134; H. von Wartenberg, *Z. physik. Chem.*, **61** (1907), 366; Bone and Coward, *J. Chem. Soc.*, **93** (1908), 1197. **93** (1908), 1975; Pring, *J. Chem. Soc.*, **97** (1910), 498; Pring and Fairlie, *Ibid.*, **99** (1911), 1796; **101** (1912), 91; also *J. I. E. C.*, **4** (1912), 812.

not strictly comparable, *i. e.*, the percentages of illuminants or saturated hydrocarbons for equal percentages of hydrogen are not the same. This is apparently due to different reactions taking place at the different temperatures and to the unequal effect of the different temperatures on the velocities of the various reactions.

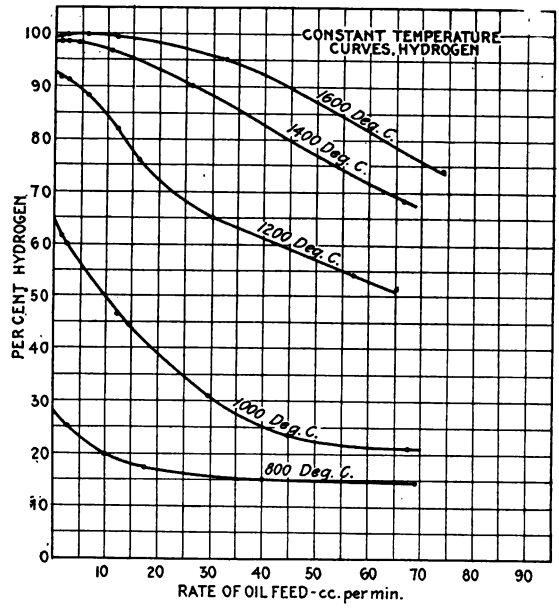
It will be noted that at low temperatures and at high rates of oil feed a decrease or increase in the oil rate has comparatively little effect on the percentages of hydrogen or illuminants in the gaseous products. This suggests that there must be a minimum percentage of each constituent at these temperatures. Yet one must not conclude from these facts that the decompositions at the low temperatures proceed in abrupt stages, as this phenomenon finds explanation in a more close consideration of the true time factor. From Fig. IX it will be seen that the rates of gas generation do not undergo material change over a considerable range of oil feed. On the assumption that the volumes of the tars in the heating zone are approximately equal, then the reaction periods for the high rates of oil feed are almost the same and should give gaseous products of similar compositions.

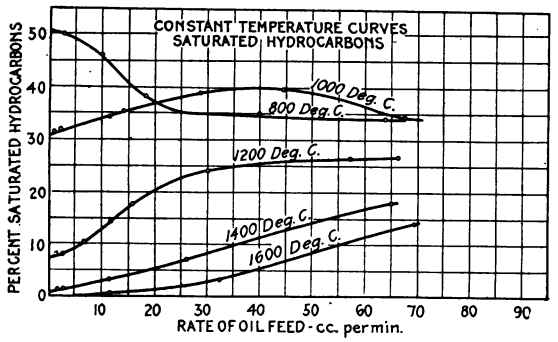
In accordance with the theoretical considerations, the maximum decomposition at any one temperature can be attained only at equilibrium, which is characteristic of an extremely long time for reaction. The curves in Fig. VII point toward such equilibrium compositions at the slow rates of oil feed. Such compositions can in all probability be attained in the heating zone at extremely slow rates of oil feed but experimental results would not verify this on account of the reversal of reactions which would take place in the cooling zone.

CHANGE OF COMPOSITION WITH TEMPERATURE AT CONSTANT RATES OF OIL FEED

In general, the constant feed curves[1] in Fig. VIII show that increase in temperature results in a greater degree of decomposition and that there are definite temperatures at which maximum and minimum percentages of the various constituents of the gas mixtures exist. The maxima for hydrogen and the minima for saturated hydrocarbons indicate to a complete decomposition of the oil into carbon and hydrogen. The

[1] Plotted from values obtained by interpolation from the curves in Fig. VII.





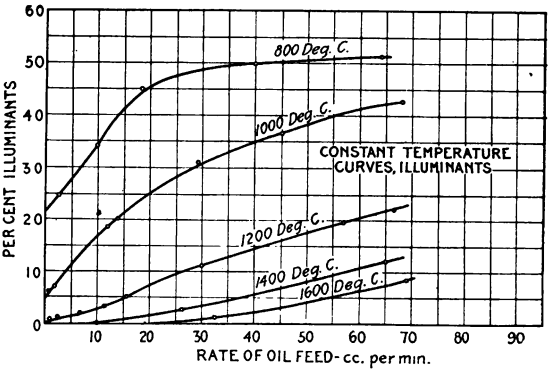


FIG. VII—CONSTANT TEMPERATURE CURVES

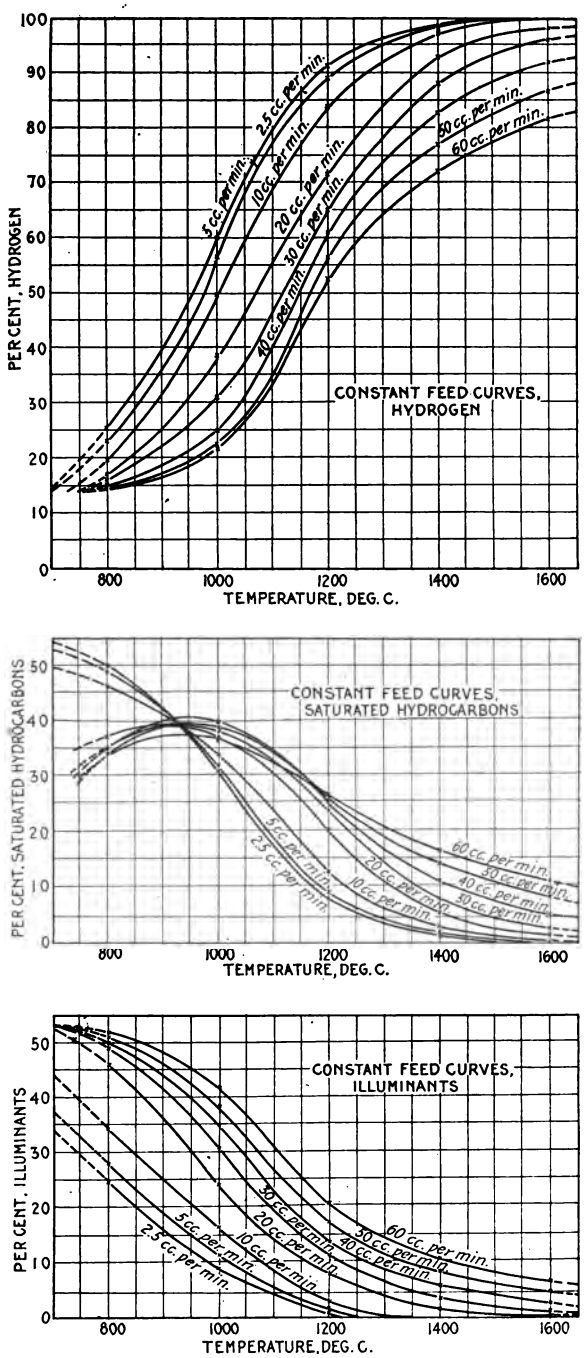


FIG. VIII—CONSTANT FEED CURVES

minima for illuminants exist at a lower temperature than the minima for saturated hydrocarbons at the same rates of oil feed, *i. e.*, in the complete thermal decomposition of hydrocarbon oils into carbon and hydrogen, the illuminants disappear before the saturated hydrocarbons. The curves for hydrogen and for illuminants seem to indicate minima and maxima, respectively, as shown by the extrapolations. On the other hand, the percentages of saturated hydrocarbons show true maxima dependent upon the rate of oil feed and the temperature.

PRODUCTION OF HYDROGEN

Table IV shows that at 1600° C., with increasing rates of oil feed, the percentages of hydrocarbons in the resulting gases decrease until a maximum of de-

TABLE IV—PRODUCTION OF HYDROGEN AT 1600° C.

Run No.	Oil rate Cc. per min.	Gas rate Liters per min.	Gas Analyses (Percentages) Illum.	H_2	C_nH_{2n+2}
1	69.0	54.0	11.8	73.1	15.1
2	32.4	34.0	1.6	96.0	2.4
3	11.5	13.0	0.0	99.2	0.8
4	6.8	8.3	0.0	100.0	0.0
5	2.4	2.9	0.0	100.0	0.0
6	0.27	....	0.2	98.6	1.2
7	0.15	....	0.7	96.8	2.5

composition is reached, when the oil is completely decomposed into carbon and hydrogen.

As stated above, under the recirculation of gas, even at 1200° C. the hydrocarbons should be completely decomposed into carbon and hydrogen, but to attain such a result at this temperature would require many minutes in the heating zone. On the other hand, this complete decomposition is realized at 1600° C. in a comparatively short reaction period, due to the great increase in the rate of decomposition at the high temperature over that at the lower temperature so that the shorter time in the heating zone is sufficient for the complete decomposition.

With any design of generator for the production of hydrogen by the direct decomposition of hydrocarbon oils, the time in the heating zone must be such as to favor complete decomposition at the desired temperature. This temperature has both a minimum and a maximum value dependent upon the principles of thermodynamics and upon practical reasons, respectively. The minimum is that lowest temperature at which equilibrium composition represents complete decomposition; *i. e.*, about 1200° C., at which temperature a long time would be necessary to complete the

reaction. The maximum is that limited by economical design and practical temperatures.

In Runs 6 and 7, made at very slow rates of oil feed, there are small percentages of hydrocarbons present. This is apparently due to a reversal of reactions as in the theoretical consideration it was concluded that if the rate of cooling was slow the reactions would reverse toward that equilibrium composition corresponding to a lower temperature.

In view of these results the range of complete decomposition is limited not only by temperature but also by definite rates of oil feed which have a maximum and a minimum limit. The maximum is that rate at which the time allowed for reaction is just sufficient for complete decomposition. The minimum is that rate at which the time required to arrest the reactions in the cooling zone is sufficiently long to cause a measurable reversal of reactions. For any temperature at which complete decomposition is possible, these limiting rates will have different values.

From these considerations it seems that the direct decomposition of hydrocarbon oils might become a future source of large quantities of hydrogen, but difficulties would be encountered in the commercial application of such a process. These obstacles would consist mainly in the economical heating of the reacting substances to the necessary high temperature and in the purification of the resulting gas. Economical heating could probably be attained by the use of a counter-current system. Purification would be necessary in order to remove the oxygen and sulfur compounds derived from the original oil.

Crossley[1] has reviewed the commercial hydrogen situation to date, but has omitted reference to the direct decomposition of oil as a possible source of hydrogen. A few patents[2] relating to such processes have been issued.

ILLUMINANTS

Table V consists of data taken from the curves of Fig. VII. These data show that it is possible to obtain gases containing equal percentages of illuminants at different temperatures by varying the rate of oil feed. At a given temperature and rate of oil feed a certain percentage of illuminants is obtained. Should it be desired to obtain a gas containing an equal percentage

[1] Crossley, *J. Soc. Chem. Ind.*, **33** (1914), 1135.

[2] Frank, U. S. Pat. 1,107,926 (1914); Ellis, U. S. Pat. 1,092,903 (1914).

of illuminants at a higher temperature, it would be necessary to increase the rate of oil feed; this is strictly in accord with the theoretical principle of reaction

TABLE V—EQUAL PERCENTAGES OF ILLUMINANTS OBTAINED AT DIFFERENT TEMPERATURES BY VARYING THE RATE OF OIL FEED

Temperatures ° C.	Oil rate Cc. per min.	COMPOSITIONS OF GASES (PERCENTAGES) Illum.	H_2	C_nH_{2n+2}
800	14.0	40.0	18.5	41.5
1000	55.0	40.0	22.0	38.0
1000	14.0	20.0	44.4	35.6
1200	57.0	20.0	53.7	26.3
1000	3.5	10.0	58.2	31.8
1200	26.5	10.0	66.5	23.5
1400	55.5	10.0	74.0	16.0
1000	1.0	5.0	63.5	31.5
1200	14.0	5.0	78.5	16.5
1400	35.0	5.0	85.5	9.5
1600	50.0	5.0	87.0	8.0

velocity that increase in temperature increases rate of decomposition and hence it should be necessary to increase the rate of oil feed (equivalent to decreasing the time for reaction) in order to obtain the same percentage of illuminants in the resulting gas. However, gases containing equal percentages of Illuminants do not necessarily contain equal percentages of the other constituents. This is apparently due to unequal effects of change of temperature on the various reactions involved in the decomposition. With a desired percentage of illuminants in view, then, it would be possible to increase materially the capacity of any oil gas generator by increasing the temperature a hundred or more degrees.

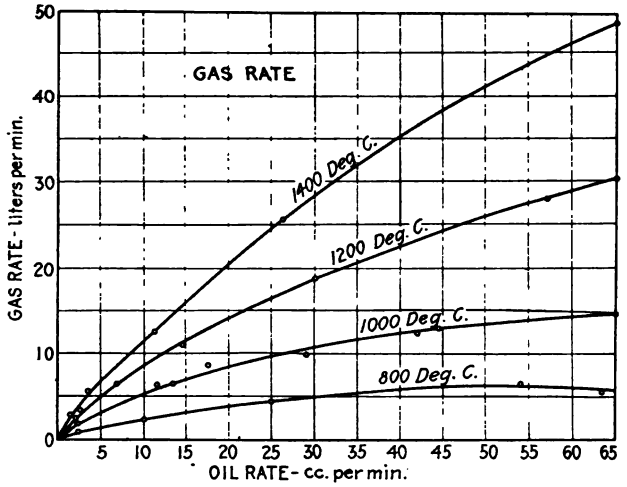
Experimentally it was found that a gas containing about 52.0 per cent illuminants could be obtained at 800° C. at a high rate of oil feed but at the same time a large amount of tar was produced.

GAS GENERATED

Fig. IX consists of two sets of curves, one showing the gas rates and the other the gas yields for the various rates of oil feed at constant temperature. The rates of gas generation and yields at 1600° C. are not shown, as runs at this temperature could not be maintained for a sufficiently long time to obtain accurate data, on account of the choking of the furnace by the large amounts of carbon formed.

The gas rate curves show that at constant temperature an increase in the rate of oil feed does not result in a proportionate increase in the rate of gas generation but rather in a decreasing ratio of gas rate to oil rate. As a result, at low temperatures and high rates of oil feed the rates of gas generation do not show a material change over a considerable range.

At 800° C. and at very high rates of oil feed the rate of gas generation actually becomes a decreasing function. This is apparently due to the checking of the course of the reactions by the insufficient time interval



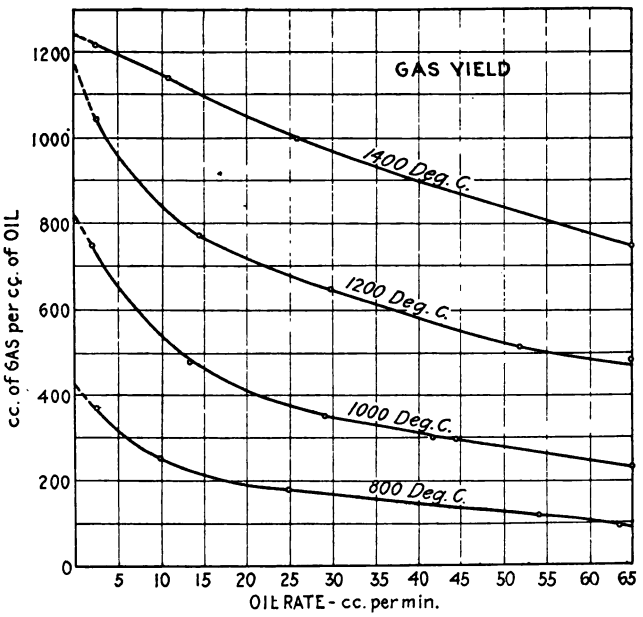


FIG. IX—GAS CURVES

allowed or to so exceeding the capacity of the furnace that the oil vapors are not heated to the temperature of the reaction zone.

The gas yield curves indicate that increase in temperature results in an increase of the yield of gas at any constant rate of oil feed. This is due to the more complete decomposition of the hydrocarbons, as shown by the compositions of the gases made at slow rate (Fig. VII). At constant temperature, decrease in the rate of oil feed will result in an increase in the yield of gas to whatever maximum is representative of the most complete decomposition to be attained at the given temperature. As stated previously a decrease in the rate of oil feed provides the longer reaction period necessary for final equilibrium. Since the most complete decomposition at any one temperature is characteristic of equilibrium composition, a maximum yield of gas can be obtained only at this final stage, although such yields of gas can not be realized experimentally on account of the above-mentioned reversal of reactions in the cooling zone.

TARS

Tar yields could not be determined with accuracy in these runs as the high rates of gas generation in many of the experiments made it impossible completely to separate the tars from the gases with the apparatus at hand. In general, the tar yield increased with increase in the rate of oil feed at a given temperature and with a decrease in temperature at constant rates of oil feed. Above 1200° C., at slow rates of oil feed, no tars were obtained. The nature of the tars obtained at the various temperatures has not been investigated.

CONCLUSIONS

I—The control of the composition of the products obtained in the manufacture of oil gas involves not only thermodynamics but also chemical kinetics.

II—In practice, equilibrium is not reached in the thermal decomposition of petroleum hydrocarbons. This is proved by the fact that a recirculation of the products, under the same conditions at which they were generated, results in a further change in composition.

III—The time factor, which is controlled by the rate of oil feed, is just as important as are the other variables (temperature, pressure and concentration), as it has been found that the compositions of the products obtained in making oil gas vary with the rate of oil feed. Hence, from the standpoint of practical

operation of an oil gas plant, the rate of oil feed offers an easily accessible means of control.

IV—Maximum and minimum percentages of the various constituents in the products formed by the decomposition of petroleum and petroleum distillates by heat can be obtained by a proper adjustment of the variables.

V—Petroleum hydrocarbons can be completely decomposed into carbon and hydrogen only within well defined limits of the four variables. In this investigation the range of complete decomposition at a definite temperature and pressure was limited by definite rates of oil feed.

VI—Oil gases containing equal percentages of illuminants can be produced at different temperatures by varying the rate of oil feed. Such gas mixtures, although they have equal percentages of illuminants, do not in general have equal percentages of saturated hydrocarbons and hydrogen, *i. e.*, gases of equal illuminating values are not necessarily of equal thermal values.

VII—In an isothermal decomposition of petroleum hydrocarbons, maximum yields of gas and minimum yields of tar are characteristic of equilibrium compositions.

VITA

Clive Morris Alexander was born in Leon, Iowa, on April 28, 1889, and there received his public school education, graduating from the Leon High School in May, 1907. He entered the State University of Iowa in September, 1907, and graduated from that institution in June, 1911, receiving the degree of Bachelor of Science in Chemistry. At the State University of Iowa, during the Summer Session of 1909, he had charge of the stock room in the department of chemistry, and during the Summer Session of 1911 was Assistant in Chemistry. He studied at Harvard University during the Summer Session of 1912. The two years 1911–2 and 1912–3 were spent in graduate work and as Assistant Instructor in Chemistry at the State University of Iowa. In June, 1913, he received the degree of Master of Science from the same institution. The following two years, 1913–4 and 1914–5, were spent in graduate study at Columbia University; during the latter year he was Goldschmidt Fellow in Chemistry.

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